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**TECHNICAL STANDARD OPERATING PROCEDURE**Date: March 27, 2000SOP No. MK-VBI70-06Title: **XRF Instrument Operation****APPROVALS:**

Author: Morrison Knudsen Corporation

Date: March 27, 2000

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SYNOPSIS: Provides procedures and instructions on the proper XRF operation protocol.

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Received by QA Unit**REVIEWS:****TEAM MEMBER****SIGNATURE/TITLE****DATE**

EPA Region 8

3/30/00

Morrison Knudsen Corp.

Ellen J. White / QA Coordinator3/27/00

REV.	DATE	REVISION DESCRIPTION
0	7/29/99	
1	3/24/00	Modification to Sections 6.0 Equipment, 7.4.1 Date Check, 7.4.2 Energy Calibration, 7.4.5 Continuing Calibration Verification, 7.4.9 Detection Limits, 7.5.1 Sample Analysis Procedures, 7.6 Data Export and Backup

MORRISON KNUDSEN CORPORATION  
Response Action Contract No. 68-W7-0039

SOP No. MK-VBI70-06

Revision No. 1

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# TECHNICAL STANDARD OPERATING PROCEDURE

## XRF INSTRUMENT OPERATION

### 1.0 PURPOSE

The purpose of this procedure is to provide instructions to Morrison Knudsen (MK) personnel assigned to the VB/I-70 project and their subcontractors on the proper XRF operation protocol.

### 2.0 SCOPE

This procedure covers activities associated with intrusive sample analysis by utilizing an energy dispersive X-ray fluorescence spectrometry method (EDXRF). The procedure details operation of the KevexSpectrace QuanX instrument, which is a field portable, but not hand held, XRF.

### 3.0 REFERENCES

Spectrace, QuanX EDXRF Analysis of Contaminated Soils Standard Operating Procedure

Spectrace, QuanX Operation Manual, Current Revision

Harding, Soil Analysis Application Report, Low Concentration Soil Contaminant Characterization Using EDXRF Analysis

Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment

### 4.0 DEFINITIONS

EDXRF: Energy Dispersive X-ray Fluorescence Spectrometer/Spectrometry  
NIST: National Institute of Standards and Technology  
ppm: Parts per million  
SRM: Standard Reference Material  
QuanX: Spectrace Brand Name for 6000 Series EDXRF



## TECHNICAL STANDARD OPERATING PROCEDURE XRF INSTRUMENT OPERATION

### 5.0 RESPONSIBILITIES

The **Field Analyst/XRF Operator** is responsible for operation and maintenance of the QuanX EDXRF and data management in accordance with this procedure.

The **Field Supervisor** is responsible for training the Field Analyst(s) on the requirements of this procedure, and for providing oversight and assistance as necessary to ensure compliance with this procedure.

The **Project Chemist** is responsible for reviewing instrument output and quality control records to confirm proper implementation of the quality control requirements.

The **Site Health and Safety Officer** is responsible for verifying the use of safe laboratory practices throughout implementation of this procedure.

The **Site Manager** is responsible for ensuring that the Field Analyst receives proper training and that proper equipment and resources are available as needed to safely operate the instrument and to generate high quality data.

### 6.0 EQUIPMENT

- QuanX EDXRF, ECD Model, equipped with spectrometer, control/pulse processing electronics, and data processor with QUANX.EXE software installed
- 20-position sample tray
- Uninterrupted Power Supply, 100-120/200-240 VAC, 5/2.5 A, 50/60 Hz, single phase, 500 watts (1000 watt total power source to support data processor)
- 3000 LE Series printer



# **TECHNICAL STANDARD OPERATING PROCEDURE XRF INSTRUMENT OPERATION**

## **7.0 REQUIREMENTS**

### **7.1 General**

A specific area within the field office will be designated as laboratory space for sample preparation and sample analysis using EDXRF. The QuanX must be supplied with power at 115V AC, 14 amps, and equipped with an uninterrupted power source. Power for both the EDXRF instrument and the personal computer should be from the same AC line. The uninterrupted power source will provide protection against power surges and allow continuous operation in the event of a power failure. This will also insure the detector remains cool and electronics stabilized, which is crucial to the EDXRF analysis. The instrument must be placed so that free air flow around the instrument is supplied, with operating temperatures of 50 - 90 degrees Fahrenheit and relative humidity less than 80%.

### **7.2 Maintenance**

Maintenance will be performed as specified in the Operations Manual, including:

- Daily Energy Calibration and Calibration Verification
- Weekly Fast Discriminator Check, Log System Status Values
- Semi-annual Interlock Test and Radiation Survey

Any maintenance performed on the instrumentation will be documented in a maintenance log. Additionally, instrument cleaning will be performed using a hand held canister of compressed air to clear dust from the instrument and data processor, in addition to wiping with a clean cloth.

### **7.3 Instrument Log**

A hardbound instrument log book will be used to record the daily instrument operations. The instrument log will be maintained in accordance with the requirements of the Technical Standard Operating Procedure for Field Documentation. Data to be entered in the logbook includes, but is not limited to, date, indoor temperature and humidity and the beginning and end of each day, time, sample ID (field, calibration or other quality control), arsenic concentration, lead concentration, and quality control sample performance.



## TECHNICAL STANDARD OPERATING PROCEDURE XRF INSTRUMENT OPERATION

### 7.4 Quality Control Procedures

7.4.1 Date Check - The system date reported with the results of the initial calibration verification will be checked each day. If the system date displayed is incorrect, type `c:\quanx\soil36c> date` and enter the correct date using the MM-DD-YY format. Repeat the initial calibration verification.

7.4.2 Energy Calibration - The energy calibration is a software function that calibrates the spectrometer electronics to assure the accuracy of the energy scale. An energy calibration will be performed daily prior to use in accordance with the manufacturer's procedures (Attachment A). If an error message appears, exit the program by pressing the F10 key.

If the error reads "ACQ Aborted: Stabilizer Lost Zero Peak," upon exiting it will ask whether to "Save Value of Gain DAC." Type N for NO. Within the Procedure Menu, follow these steps:

1. Press the F7 key again to start the energy calibration, pause for approximately 20 seconds and press the space bar to start the program. Repeat this procedure if no response is received.
2. If the first procedure does not work, exit the program by pressing the F10 key. Type `c:\quanx\soil36c> cd` and press Enter, repeat to obtain the c: prompt. Turn the unit off, then on and wait approximately one minute. Type `cd quanx` press Enter, then `cd soil36c` and press Enter. Type **Quanx** to reach the Procedure Menu. Press the F7 key and pause, then press the space bar to start the program.
3. Re-run the Energy Calibration
4. If the error persists, hit the space bar to return to main menu. Select "Low Z Unknown," pres F2 (set-up), and verify both the Acquisition Parameters and the Spectrum Processing values against the parameters as defined in Section 11 of the Spectrace Software Manual (Chapter 11). Re-set any values that vary from those defined in the Manual. Press F10 to return to the main menu, select "Mid Z Unknown" and repeat this verification for the Mid Z range.
5. Re-run the Energy Calibration



## TECHNICAL STANDARD OPERATING PROCEDURE XRF INSTRUMENT OPERATION

6. If the error persists, contact the Field Supervisor. The Field Supervisor will review and may repeat the troubleshooting procedures with the Analyst, and will contact the Kevex Spectrace Representative if Energy Calibration cannot be achieved. If the instrument is out of operation due to calibration failure or other problems for more than 24 hours, then the Site Manager and EPA Remedial Project Manager will be notified.

7.4.3 Initial Calibration Verification - MK will utilize a Fundamental Parameter method to check the instrument calibration using the following three standard reference materials (SRM), or equivalent:

- SRM 2709 San Joaquin Soil (Baseline Trace Element Concentrations)
- SRM 2710 Montana Soil (Highly Elevated Trace Element Concentrations)
- SRM 2711 Montana Soil (Moderately Elevated Trace Element Concentrations)
- SRM 8704 Buffalo River Sediment (not certified for As, to be used on trial basis)

Only SRM that have been certified by the National Institute of Standard and Technology shall be utilized, and all certifications shall be reviewed and maintained. The initial calibration verification check will be performed by analyzing the three standards each day, simultaneously, following the energy calibration and prior to analysis of environmental samples. Results will be compared against the acceptable concentration ranges of 80 - 120% of the certified value (acceptance criteria apply to concentrations above the MDL only). If one or more concentrations fall outside of the acceptable concentration ranges, the SRM will be re-analyzed. If the results remain outside of the acceptable concentration ranges following three runs, refer to Troubleshooting Procedures, which include a standardization test if necessary, to be performed as specified in the Operations Manual. Prior to proceeding to the standardization test, the following procedures may be performed:

- Turn the sample cup with mylar facing up and tap the container to loosen the soil from the mylar. Shake the sample from side to side and turn back over with mylar facing down, tap on paper towel and place in tray for re-analysis; or
- Replace the mylar.



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Environmental samples will not be analyzed without verifying acceptable instrument calibration.

- 7.4.4 Standardization Test - If the calibration cannot be achieved following the Troubleshooting Procedures, the instrument will be re-standardized. From the Procedure Menu, select "SOIL STANDARDS 6+7". Press the F1 key and the program will prompt you to place each SRM in a designated position. Press the space bar to start the program. The printout from this test will be retained and noted in the instrument log; however, the standardization test results will need to be removed from the downloaded electronic data. If the calibration cannot be achieved following re-standardization, the Field Supervisor will be contacted. The Field Supervisor will review and may repeat the troubleshooting and standardization procedures with the Analyst, and will contact the KevexSpectrace Representative if calibration problems persists. If the instrument is out of operation due to calibration failure or other problems for more than 24 hours, then the Site Manager and EPA Remedial Project Manager will be notified.
- 7.4.5 Continuing Calibration Verification - One SRM check standard will be included with the environmental samples for every sample run. The SRM result will be verified against the NIST acceptable concentration range between each run. If the result is not within the acceptable range (80 - 120% of the certified value for concentrations above the MDL), troubleshooting procedures will be performed as described in 7.4.3 and 7.4.4, and the associated samples will need to be re-analyzed along with the SRM.
- 7.4.6 Blank Samples - Method blanks and instrument blanks will be prepared and analyzed using clean silica sand or other material specified in Method 6200. The instrument blank will be run once per every 20 samples. A method blank will be run at least daily to monitor for contamination that may have been introduced through the sample preparation. The method blank is subject to the same preparation procedures as the environmental samples. Detections in the instrument blank or method blank will require that the problem be identified and corrected prior to running additional field samples. Samples analyzed with a blank containing detected elements must be re-analyzed.



## **TECHNICAL STANDARD OPERATING PROCEDURE XRF INSTRUMENT OPERATION**

- 7.4.7 Performance Evaluation Samples - Performance evaluation samples may be analyzed to assess system performance. All performance evaluation samples will be identified and packaged in the same manner as environmental samples and submitted blind to the analyst.
- 7.4.8 Field Laboratory Duplicates - Duplicates consist of two samples extracted from one source. Laboratory duplicates will be prepared following the sample preparation by placing the prepared soil in two XRF cups and labeling one with the sample ID followed by "DUP". Laboratory duplicates will be analyzed in the same run. Results of the duplicates will be reviewed by the analyst immediately following analysis to evaluate system performance. The RPD will be calculated and entered into the instrument log. The relative percent difference (RPD) should not exceed 20% or, alternatively, the absolute difference should not exceed the MDL. If these limits are exceeded, actions should be taken as described in the Project Plan QAPP, Table 4-2.
- 7.4.9 Detection Limits - The AR Harding Soil Analysis Application Report (attached) presents the lower levels of detection applicable to the QuanX EDXRF (Spectrace 6000) equal to 12 ppm for arsenic and 7 ppm for lead. A detection limit study will be performed as described in Method 6200 and 40CFR Part 136, Appendix B to confirm instrument-specific sensitivity on site-specific soil. Analysis will be performed on seven aliquots of a homogenized low-concentration site-specific soil sample with arsenic and lead concentration between 1 and 5 times the expected method detection limit (As: 12 - 60 ppm, Pb: 7 - 35 ppm). The method detection limit will be defined as 3 times the standard deviation of the seven measurements. The MDL study will be repeated several times throughout the course of the project and the results will be plotted.

### **7.5 Sample Analysis Procedures**

- 7.5.1 Inspect prepared samples to verify condition and proper identification.





## TECHNICAL STANDARD OPERATING PROCEDURE XRF INSTRUMENT OPERATION

- 7.5.2 Enter sample identification into XRF log book (**maximum 18 samples per run, plus one laboratory duplicate and one standard**), and enter the instrument blank and check standard identifications used for that run into log book. NOTE: (alternate check standards for each run.)
- 7.5.3 Open QuanX cover and load samples into sample tray, matching the log book sequence to the tray numbers. To load samples, tap each sample mylar facing down on a clean paper towel. Place sample in tray with mylar facing down so that the sample sits level. **Re-check that log book sequence number matches tray number for each sample.**
- 7.5.4 Close QuanX cover.
- 7.5.5 From the Procedure Menu screen - select "SOIL UNKNOWN 2+3".
- 7.5.6 Press the F1 key to prompt "HOW MANY SAMPLES TO RUN?" Type in total number (including check standard and method blank if present) from log book and hit enter. From the sample identification screen, enter identifications from log book and press Enter after each entry. **Prior to pressing Enter following the last sample identification, re-check the sample identification entries against the log book.**
- 7.5.7 Press the final Enter, and the instrument will automatically start the sample analysis.
- 7.5.8 If an error is discovered, cancel this program by pressing the F10 key, make the necessary corrections and repeat the procedure.
- 7.5.9 Upon completion of analysis, the QuanX will automatically begin to print the results. The printout will report the elements analyzed, concentration in ppm, and error for each sample identification. Record the concentration of arsenic and lead results in the instrument log book and review quality control sample results as discussed in Section 7.6.



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### 7.6 Data Export and Backup

The data will be exported daily at the beginning of each day for the previous completed day of analysis. A daily backup of all data will be maintained.

The instrument-generated SPC and RESULTS data files will be downloaded. The SPC file contain the run date, run time and coded spectrum for each sample identification. The RESULTS file is an ascii text file containing the run date, run time, sample identification, element, results, units, and instrument-calculated error. The export will be performed as follows:

1. Press **F10** to exit QuanX program
2. Open **MSWindows Explorer** program
3. Open the data directory, currently *c:\quanx\soil36c*
4. Select **RESULTS** file and note file size
5. Insert floppy disk into drive a: and copy **RESULTS** file to a:
6. View file size on a: to verify complete file transfer
7. Select **SPC** file
8. Zip and copy **SPC** file to a:
9. Rename RESULTS file to **RESymmdd**, where ymmdd is the last digit of the year, and the month and date of the analytical run date
8. Rename SPC.zip file to **SPCymmdd.zip**
9. Delete **RESULTS** and **SPC** files from *c:\quanx\soil36c*
10. Copy **RESymmdd** from a: onto networked computer hard drive directory designated for the current program phase (*c:\RES<programID>*)
11. Label floppy disk with the date range of contents and file names, and file as a back-up copy in a secure location at the field office
12. E-mail **RESymmdd** file to Project Chemist or designee at office
13. The Project Chemist or designee will extract the file to the designated secure project data directory
14. XRF Results files will then be forwarded for conversion, review, and uploading to the project database as directed by the Database Manager



# **TECHNICAL STANDARD OPERATING PROCEDURE XRF INSTRUMENT OPERATION**

## **8.0 RECORDS**

- NIST Certificates of Analysis for Each Standard Reference Material
- Instrument Log Book
- Maintenance Log
- Electronic and Hard Copy Instrument Data

## **9.0 ATTACHMENTS**

- A Spectrace QuanX Laboratory X-Ray Fluorescence Analyzer Standard Operating Procedure
- B Soil Analysis Application Report: Low Concentration Soil Contaminant Characterization Using EDXRF Analysis



**TECHNICAL STANDARD OPERATING PROCEDURE  
XRF INSTRUMENT OPERATION**

**ATTACHMENT A**

**Spectrace QuanX Laboratory X-Ray Fluorescence Analyzer  
Standard Operating Procedure**



## STANDARD OPERATING PROCEDURE

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# SPECTRACE QuanX EDXRF ANALYSIS of CONTAMINATED SOILS

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# SPECTRACE QUANX LABORATORY X-RAY FLUORESCENCE ANALYZER STANDARD OPERATING PROCEDURE

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# SPECTRACE QUANX LABORATORY X-RAY FLUORESCENCE ANALYZER STANDARD OPERATING PROCEDURE

## 1.0 Scope and Application

This document addresses the application of energy dispersive X-ray fluorescence spectrometry (EDXRF) to the determination of contaminant metals in soil and sediments. The EDXRF technique is capable of both qualitative and quantitative analysis of elements with atomic numbers 11 (sodium) through 92 (uranium). This operating procedure discusses the determination of the elements listed in Table 1.

Table 1. Elements and their atomic symbols analyzed by the EDXRF method.

Arsenic (As)	Manganese (Mn)
Barium (Ba)	Mercury (Hg)
Cadmium (Cd)	Nickel (Ni)
Calcium (Ca)	Potassium (K)
Chromium (Cr)	Silver (Ag)
Copper (Cu)	Titanium (Ti)
Iron (Fe)	Zinc (Zn)
Lead (Pb)	

## 1.1 Principles of Operation

The Spectrace QuanX is a benchtop mounted, laboratory grade EDXRF instrument. A one, ten or twenty position sample changer is available for sample analyses.

### 1.1.1 Fundamentals of the X-ray spectrometric measurements

The basis of X-ray fluorescence spectrometry is the interaction of X-rays produced by the Spectrace QuanX X-ray tube with the constituents of the soil or sediment sample.

When atoms in a soil sample absorb the tube x-radiation, the energy causes the ejection of an electron from the atomic cloud. Next, electronic transitions occur to return the excited atom to a ground energy state. These transitions result in emission of a *characteristic X-ray*. The energy of the characteristic X-ray indicates the atomic number of the emitting atom and the specific electronic transition that occurred. (Reference 1,2)

The lithium drifted silicon (Si(Li)) detector converts the characteristic X-ray energy into an electronic signal. The electronics in the Spectrace QuanX further processes the signal and displays the X-ray spectrum on a personal computer.

### 1.1.2 Generation of spectral background

When the X-ray tube shines on the soil sample, some of the X-rays are scattered toward the detector rather than absorbed by the soil. The X-ray spectrum then shows the scattered radiation as background under the elemental emission lines. The magnitude of the background limits the achievable minimum detectable limit for the target contaminant elements.

The peak fitting and deconvolution software of the Spectrace QuanX filters background signal prior to quantitative analysis. Each soil spectrum then can be compared with another without regard to background variations.

## 2.0 Overview of the method

Three spectra are acquired for each EDXRF measurement. Each spectrum optimizes one or more target elements or matrix constituents of the sample. Standardization of the EDXRF method relies on National Institutes of Standards and Technology (NIST) certified soil standard materials.

Elemental emission peak deconvolution is followed by quantitative analysis with a fundamental parameters method. The fundamental parameters method can accurately determine the composition of a sample even though the standards used do not cover the range of concentrations expected. Additionally, fundamental parameters can address matrix interactions from widely varying soil types.

Calibration by fundamental parameters proceeds by completely defining for the program each standard sample's composition, including the major components (ex. Fe, Ca). Many instances arise when a portion of the matrix may be better estimated by a difference component. For soil, the difference component is defined as  $\text{SiO}_X$  where X can be 2 - 5. When X = 5, a composition of 24% Si and 45% O results that approximates the concentrations found in most soils types.

The tube output distribution is calculated by the program followed by determination of the matrix independent pure element count rate (PECR) for each analyte. The routine then develops a set of theoretical standards. Next, the routine computes the theoretical X-ray intensity expected for each analyte using the Sherman (Reference 3) formula

$$I_L = \omega_A g_L \frac{r_A - 1}{r_A} \frac{d\Omega}{4\pi} \int_{E_{abs}}^{E_{max}} \frac{I_E C_A \mu_A(E) \csc \phi}{\mu_M(E) \csc \phi + \mu_M(E_A) \csc \psi} dE \quad \text{Eq. 2.1}$$

where:

$I_L$  - intensity of the analyte emission line;

$\omega_A$  - fluorescent yield of analyte A;

$g_L$  - fractional value of the measured analyte line (L) in its series;

$r_A$  - absorption edge jump ratio of analyte A;

$\frac{d\Omega}{4\pi}$  - fractional value of the fluorescent X-ray that is directed toward a detector;

$E_{max}$  - maximum tube output X-ray energy;

$E_{abs}$  - absorption edge energy of analyte A;

$I_E$  - intensity of the primary X-ray beam at energy (E);

$C_A$  - concentration of analyte A;

$\mu_A(E)$  - mass absorption coefficient on analyte A for X-ray energy (E);

$\phi$  - incident angle of primary beam;

$\mu_M(E)$  - mass absorption coefficient of the matrix for X-ray energy (E);

$\mu_M(E_A)$  - mass absorption coefficient of the matrix for analyte X-ray;

$\psi$  - take off angle of the fluorescent emission.

Combining the theoretical standard and intensity information, alpha influence coefficients are determined by solving simultaneous equations of the form developed by Lachance and Traill (Reference 4) shown in equation 2.2 below. Alpha coefficients describe the quantitative effect of each matrix element on an analyte's measured X-ray intensity.

$$C_i = B_i + K_i I_i (1 + \sum_{j=1}^n \alpha_{ij} C_j) \quad \text{Eq. 2.2}$$

where:

- $I_i$  = X-ray intensity of element i;
- $\alpha_{ij}$  = alpha coefficient describing the matrix interaction of element j on analyte i;
- $C_i$  = concentration of analyte element i;
- $K_i$  = slope term;
- $B_i$  = intercept term;
- $C_j$  = concentration of matrix element j.

Unknowns are quantified by estimating analyte concentration from the measured intensity and the alpha coefficients. Next, theoretical intensities are calculated from equation 2.1 and compared to the measured intensities. If the intensities are more than 1% different, a new estimate of concentration is made and the theoretical intensity computation is repeated. The iteration continues until the theoretical and measured intensities converge (Reference 5).

### 3.0 Sample containers and handling

After sample collection by EPA approved protocol, samples should be stored in either metal free glass jars or polyethylene bags. In the lab, only disposable wooden or plastic spatulas and clean glass drying containers should contact the soil samples.

### 4.0 Interferences

The EDXRF method is a total elemental analysis technique. Errors can arise for the following sources:

#### 4.1 Sample preparation error

The nature of soil samples require an approach to such variables as moisture, particle size, and heterogeneity and representitiveness of the sample to the soil at the site. Sample preparation as outlined in this SOP minimizes or eliminates the effects of many of these variables on the EDXRF result.

#### 4.2 Spectral interference

Emission line overlap can be severe depending on the spectral peak position and relative concentrations of the overlapping elements. The Spectrace software utilizes a multiple linear least squares deconvolution method that provides accurate analyte peak intensities for subsequent quantification.

##### 4.2.1 Lead [Pb] L $\alpha$ line and arsenic [As] K $\alpha$ line overlap

Accurate peak deconvolution is obtained at lead concentration to arsenic concentration ratios of 17:1 (Reference 6).

#### 4.3 Chemical matrix interferences

Quantitative X-ray fluorescence analysis is a comparison analytical method; EDXRF spectrometer response for an elemental emission line is evaluated with respect to the known concentration of the element in a standard material. Contaminated soils are complex samples in regard to their overall elemental composition. Matrix effects are defined as the impact that the concentration variations of major soil components (ex. Ca, Fe, Si) has on measured analyte X-ray emission intensity.

The fundamental parameters method mathematically corrects analyte intensities with respect to concentration variations of sample matrix components

## 5.0 Equipment and apparatus

### 5.1 Description of the Spectrace QuanX

The Spectrace QuanX is a benchtop mounted, laboratory grade, energy dispersive X-ray fluorescence (EDXRF) spectrometer. It has found wide application in the analysis of soils, sediments, hazardous waste, and waste oil materials.

The instrument utilizes a high flux rhodium [Rh] or tungsten [W] anode X-ray tube which is positioned to direct X-rays onto the sample. Standard equipment includes a liquid nitrogen cooled lithium drifted silicon [Si(Li)] solid state X-ray detector. Optionally, an electronically cooled Si(Li) detector could be substituted.

Pulse processing electronics in the Spectrace QuanX chassis communicate spectral data to a personal computer. The personal computer displays and processes spectral information, and outputs elemental concentration data.

### 5.2 Equipment and apparatus list

#### 5.2.1 Spectrace QuanX Analyzer System

The complete Spectrace QuanX Analyzer system includes:

- Spectrace QuanX cabinet
- Spectrace QuanX operators manual
- Personal computer (a 486 is recommended) with QUANX.EXE software installed and a printer.
- Spectrace QuanX technical manual

#### 5.2.2 Sample preparation and presentation materials

- Sample comminution device - mechanical grinder (tungsten carbide) or manual grinding device - mortar and pestle (tungsten carbide)
- Drying oven - conventional (115 degrees Celsius) or microwave
- 10 mesh brass sieve
- Drying containers (glass or polyethylene)
- Disposable X-ray cups (32 mm outside diameter)
- Polypropylene window film (0.25 mil thickness)

#### 5.2.3 Limits and Precautions

Spectrace QuanX operators are protected from accidental exposure to X-rays by a lid lock and interlocks on all covers. If any problems arise with the X-ray on indicator light on the front panel or with the interlock system contact your Spectrace Instruments service engineer.

Beryllium windows are present on the X-ray tube and detector. Do not allow any sample or debris to fall on the window to avoid puncturing it. If a window should break note the beryllium metal is poisonous. Use extreme caution when collecting broken beryllium pieces. Consult your Spectrace Instruments service engineer for advice on cleanup of broken windows.

Liquid nitrogen detectors require periodic replenishing of the cryogenic liquid. Contact of cryogenic liquids to skin can be dangerous. Wear loose fitting, insulating clothing and avoid spilling the liquid nitrogen.

### 5.3 Instrument maintenance

#### 5.3.1 Detector cooling

If a liquid nitrogen cooled detector is employed, refill the dewar every 7 days or more frequently if required.

If the Spectrace QuanX is equipped with an electronically cooled detector, ensure the free flow of air around the spectrometer cabinet. Additionally, a supply of uninterruptable 110V AC power is recommended.

#### 5.3.2 Sample chamber cleaning

Keep debris and dust wiped from the chamber. Do not use forced air to dust the chamber because the detector beryllium window is fragile.

### 6.0 Reagents

A first step in the determination is to acquire a library of reference peak shapes for emission peak deconvolution.

#### 6.1 The following reagents for the acquisition of peak shape spectra:

Potassium carbonate	Tungsten oxide
Calcium carbonate	Mercury oxide
Titanium dioxide	Lead oxide or metal
Vanadium oxide	Arsenic oxide
Chromium oxide	Rubidium carbonate
Manganese oxide	Strontium carbonate
Iron oxide	Zirconium oxide
Copper metal	Silver metal
Cobalt oxide	Cadmium metal
Nickel metal or chloride	Tin metal
Zinc metal or oxide	Antimony oxide
	Barium carbonate

All compounds or metals should be Analyzed Reagent grade or better.

## 6.2 Interference sample

When lead [Pb] metal or oxide is used to produce the reference lead emission lines the  $L\alpha$  and  $L\beta$  ratio does not accurately reflect the ratio found in soil spectra (Reference 6). For this reason, an interference sample is used to generate the lead reference spectrum.

### 6.2.1 Composition of interference sample

Boric acid [ $H_2BO_3$ ] - 15.8%  
Silicon dioxide [ $SiO_2$ ] - 50%  
Aluminum trioxide [ $Al_2O_3$ ] - 20%  
Calcium oxide [ $CaO$ ] - 11%  
Iron oxide [ $Fe_2O_3$ ] - 1%  
Iron metal [Fe] - 2%  
Lead nitrate [ $Pb(NO_3)_2$ ] - 0.2%

### 6.2.2 Formulation of the interference sample

The materials listed in section 6.2.1, weighed to proper proportions, are introduced into a mechanical grinding vessel and ground for 3 minutes. This material is available from the Spectrace Instruments Applications Department upon request.

## 7.0 Procedures

### 7.1 Prerequisites

#### 7.1.1 Site location

The instrument must be placed so that free air flow around the instrument is supplied. Operate at temperatures of 50 -90 degrees Fahrenheit and relative humidity between 20 - 80% only. Power requirements are 115 V AC, 14 amps and a power conditioner/filter is recommended. Power both the Spectrace QuanX instrument and the personal computer from the same AC line.

#### 7.1.2 Detector cooling

Two modes of Si(Li) cooling can be employed. If a liquid nitrogen cooled detector is used, the dewar must be replenished with liquid nitrogen every seven days or as needed.

Electronically cooled detectors require AC power during operation, however, Spectrace Instruments recommends continuous power to the system so that the detector remains cool and electronics stabilized.

#### 7.1.3 Energy calibration

Once every twenty four hours, the gain setting of the instrument must be checked using the copper calibration disk supplied by the manufacturer. Execute the automated "ENRGY CALIB" function from the procedure menu. The computer automatically adjusts electronics gain to ensure proper calibration. This function normally takes between 8 and 10 minutes. Figure 1 shows the copper emission spectrum displayed during energy calibration.

#### 7.1.4 Acquisition of reference peak shape spectra

The acquisition of reference spectra is only required once. As long as no pulse processing modules have changed, these peak shape references remain valid. Often, this procedure can be done at the manufacturers site.

Place the materials listed in section 6.1 and the interference sample described in section 6.2 in individual X-ray cups with polymer window film seals. Then acquire the following spectra in a subdirectory labeled \REFS with the conditions listed below. Reference is made to DOS file naming structure below. Consult Chapter 4 of the Operators Manual or a DOS manual.

- 10 kV, aluminum filter, - for the elements potassium, calcium, titanium, vanadium, chromium, and iron. Save the spectra individually in the \REFS subdirectory with the spectrum number equal to the atomic number (i.e. potassium [K] - SPECTRUM.19). Place the cursor on the  $K\alpha$  peak of each element emission and allow at least 30,000 counts to acquire in the channel.
- 35 kV, thick palladium filter - for the elements cobalt [Co], nickel [Ni], zinc [Zn], bromine [Br], arsenic [As], rubidium [Rb], strontium [Sr], and zirconium [Zr]. Save the spectra individually in the \REFS subdirectory with the spectrum number equal to the atomic number (i.e. cobalt [Co] - SPECTRUM.27). Place the cursor on the  $K\alpha$  peak of each element emission and allow at least 30,000 counts to acquire in the channel. For the L line emission of mercury [Hg], lead [Pb], and tungsten [W] allow at least 10,000 counts to acquire in the  $L\alpha$  channel. Save the spectrum as 100 + the atomic number (mercury [Hg] - SPECTRUM.180). For the interference sample, use the same conditions as above but allow the spectrum to acquire for 1000 seconds livetime and save the spectrum as SPECTRUM.199.
- 48 kV, thin copper filter - for the elements silver [Ag], cadmium [Cd], tin [Sn], antimony [Sb], and barium [Ba]. Save the spectra individually in the \REFS subdirectory with the spectrum number equal to the atomic number (i.e. silver [Ag] - SPECTRUM.47). Place the cursor on the  $K\alpha$  peak of each element's emission line and allow at least 30,000 counts to acquire in the channel.

## 7.2 Standardization of the Method

Standardization of the Spectrace QuanX uses a set of NIST certified reference materials and/or site specific calibration standards. By using these materials, the EDXRF standardization then can be referenced to NIST certificates or an independent analysis referee method. Standardization adjustment can be affected by including or omitting a particular analyte element in a standard or addition or removal of a standard sample altogether.

### 7.2.1 Setting up the standards file

For the standards NIST 2709, 2710, 2711, 2704, 8407, 8408 type in the standards file as shown in Figure 2. Parentheses indicate that the concentration is to be used to define the matrix of the standard but not to be used for estimation of analyte sensitivity. Generally, those concentrations in the standard less than 50 ppm are defined in parentheses. A blank indicates that the component is either not present or is at a concentration near the minimum detectable limit of the method. Consult the Spectrace Instruments Fundamental Parameters software manual for further details.

### 7.2.2 Setting up the reference and spectrum processing file.

Enter the reference file following the instructions in Chapter 4 of the Spectrace Instruments QuanX users manual.

7.2.3 Set up the analysis technique menu in the combination procedure, see setup of multiple procedures in Chapter 4 of the Spectrace QuanX operators manual.

7.2.4 Set up the acquisition conditions as follows:

Low Z procedure: 10 kV tube voltage, 0.70 mA tube current, aluminum (0.13 mm) filter, and 100 seconds analysis livetime. Figure 6 is an example of a Low Z acquired spectrum.

Mid Z procedure: 35 kV tube voltage, 0.12 mA tube current, thick palladium [Pd] filter (0.13 mm), 200 seconds analysis livetime. Figure 7 is an example of a Mid Z acquired spectrum.

High Z procedure: 48 kV tube voltage, 0.10 mA tube current, thin copper filter (0.37 mm), 200 seconds analysis livetime. Figure 8 is an example of a High Z acquired spectrum.

7.2.5 Run the analysis of the standards.

7.2.6 Evaluation of the standardization:

Table 2 lists the pure element count rates for the standardization. The pure element count rates should be within 20% relative of these values.

Table 2. Pure element count rates for the elements analyzed.

Element	Pure Element Count Rate	Element	Pure Element Count Rate
Arsenic	55255	Manganese	33990
Barium	12071	Mercury	6115
Cadmium	27123	Nickel	26386
Calcium	10665	Potassium	6795
Chromium	30341	Silver	27115
Copper	25583	Titanium	18365
Iron	34186	Zinc	28131
Lead	9450		

7.2.7 Set up three procedures for the analysis of unknowns, identical to steps 7.2.2 to 7.2.4 except indicate a combination procedure in the mode "Run unknowns" in the analysis technique menu. Figure 9 is an example of a Spectrace QuanX soil sample unknown printout.

### 7.3 General keys and menu software

The Spectrace Instruments Operators manual and Fundamental Parameters software manual should be consulted for operation and flow of analysis of the Spectrace software.

### 7.4 Pre operational checks

#### 7.4.1 Control sample check

One of the six NIST soil standards or a well characterized sample from the site is analyzed as an unknown. Plot the concentration response for at least one element (preferably a target analyte) from each of the three acquisition conditions on a control chart. For those analytes with greater than 100 ppm concentration, the result should be within 20% of the known



elemental concentration. If a result exceeds the 20% limit, restandardize the method as described in section 7.2.

If more than one measurement of an element in a set of five exceeds the Upper or Lower control limit ( $\pm 3 \times$  standard deviation of the charted data) perform a resolution and stability check.

#### 7.4.2 Resolution and stability check

A resolution and stability check should be performed if the test outlined in section 7.4.1 fails. See the sample output in Figure 10 or consult the Spectrace Instruments Model QuanX Technical manual for details. Contact a Spectrace service engineer if the instrument fails this test.

### 7.5 Analysis of unknown soil samples

7.5.1 Prepare samples as indicated in Section 8.0.

7.5.2 On the procedure menu, select the run unknowns combination procedure setup in Section 7.2.7.

7.5.3 Hit the F1 "RUN" key and enter the number of samples to analyze and the identifying label for the first soil sample. Repeat for all individual samples in the set to be analyzed. Figure 9 is an example of a Spectrace QuanX soil sample unknown printout.

### 7.6 Minimum Detectable Limits (MDL's) of the method for the Spectrace QuanX

#### 7.6.1 Non target elements method MDL's

Determination of the non-target elements' MDL's proceeds by averaging the counting statistic error from the "CONCENTRATION ERROR" printout header for the element in each of the six standards. This average, multiplied by 3 is the MDL reported for that element.

#### 7.6.2 Target elements MDL's

For the target elements, select the NIST standard which comes closest to the action level concentration for the target. Then using the "PEAK BACKGROUND" printout format use equation found in section 8.1 to determine MDL's.

7.6.3 Typical MDL's for the Spectrace QuanX for soils are listed below in Table 3.

Table 3. Minimum detectable levels of EDXRF analyzed elements.

Element	MDL (mg/kg)	Element	MDL (mg/kg)
Arsenic	8	Manganese	12
Barium	35	Mercury	8
Cadmium	2	Nickel	7
Calcium	90	Potassium	120
Chromium	16	Silver	2
Copper	4	Titanium	18
Iron	11	Zinc	4
Lead	4		

## 8.0 Sample preparation

- 8.1 First agitate the sample in its glass or bag container to mix the soil material.
- 8.2 Using a wooden spatula, transfer approximately 15 grams of sample material onto the glass drying container.
- 8.3 Place in the drying oven and drive off moisture.
- 8.4 Sieve dried material through 10 mesh screen and discard the fraction held in the screen.
- 8.5 Transfer the material passing through the screen to the grinding vessel and grind for a preset period of time to assure -250 mesh material.
- 8.6 Transfer approximately 8 grams of the dried material into a labeled disposable X-ray cup and seal with one sheet of polypropylene window film.

## 9.0 Calculations

### 9.1 MDL calculation for non-target elements

Calculation of the MDL for the non-target elements is three times the average counting statistics error. Use the "CONCENTRATION ERROR" report format to obtain the data.

### 9.2 MDL calculation for target elements

Calculation of the MDL for the target elements uses Equation 9.1 below and requires peak and background counting data from an NIST certified soil standard reference material containing a concentration of the target element closest to the predetermined action level. Use the report format "PEAK BACKGROUND" to obtain the data for this calculation.

$$MDL = \frac{3 \times \sqrt{B}}{P} \times conc. \quad \text{Eq. 9.1.}$$

Where the variables are defined as:

MDL - minimum detection level;

B - background counts under fitted analyte peak;

P - fitted peak counts of analyte peak;

conc. - concentration of analyte from standard reference material certificate provided by NIST.

### 9.3 Minimum Quantitation Level (MQL)

The minimum quantitation level (MQL) is the concentration of analyte required to ensure a measurement precision of 10% relative standard deviation. Equation 9.2 illustrates the calculation of MQL.

$$MQL = 3 \times MDL \quad \text{Eq. 9.2.}$$

## 10.0 Quality assurance/quality control

### 10.1 Precision

Precision data is accumulated in the pre-operational check listed section 7.4. Figure 7 lists typical analytical precision for NIST 2710. Keep in mind that precision is a function of counting time and the number of peak counts and background counts collected for the analyte. Precision in EDXRF measurements is predicted by counting statistics as shown in the following equation:

$$Rel. \sigma_{theo} = \frac{\sqrt{P + 2 \times B}}{P} \times 100\% \quad \text{Eq. 10.1}$$

The Spectrace Instruments model QuanX typically provides measurement precision (indicated by the control chart plotted in section 7.4) 1.2 - 1.8 times the  $\sigma$  theoretical. Several acquisitions of the control sample are required prior to making this determination.

### 10.2 Accuracy

The accuracy of an EDXRF measurement can be verified in two ways. First, certified soil reference materials (procured from the NIST or other standard generating entity) not utilized in the Spectrace QuanX standardization are analyzed as soil unknowns as outlined in Section 7.5. Verify that results for target elements near the predetermined action concentration level are within 20% of the certified concentration for the standard.

Second, a subset of samples (10% at the minimum), preferably near the action concentration level, are submitted to a laboratory for acid digestion and ion-coupled plasma emission or atomic absorption spectrometric (ICP/AA) analysis. The split submitted should be taken of the prepared soil material subsequent to Section 8.5. Target elements exhibiting a regression analysis (EDXRF data versus ICP/AA data)  $r^2$  value greater than 0.95 have been considered QA3 level data. Regression analysis producing  $r^2$  values of 0.7 or above can be considered QA1 level (field screening) data. To improve the  $r^2$  value, ICP/AA analyzed soil materials maybe added to the standards file setup in 7.2.1. The utmost discretion should be used to alter the standardization method of section 7.2. Laboratory data should be provided for all the elements listed in the standards file (Figure 2). Short of that potassium, calcium and iron along with the target elements must be determined in the potential site specific standard samples.

#### 10.2.1 Matrix considerations

Complimentary QA/QC verification include analysis of soils with varying matrix composition. Of interest is the effect on EDXRF results when analyzing samples with high siliceous or calcareous soils or soils with high iron composition.

Additionally, acid digestion and ICP/AA analyzed site specific standards can introduce error due to variable recoveries, caused by soil matrix differences, of target elements. When site specific standards are used, errors are propagated into the EDXRF standardization. For a discussion of site specific standardization see Reference 7 and the addendum to this SOP.

## 11.0 References

- (1) E.P. Berin, "Principles and Practice of X-ray Spectrometric Analysis", 2nd ed., Chap. 2, Plenum Press, New York (1975).
- (2) J.L. de Vries, B.A.R. Vrebo, "Handbook of X-ray Spectrometry", R.E. Van Grieken and A.A. Markowicz, eds., Chap. 1, Marcel Dekker (1993).
- (3) J. Sherman, Spectrochimica Acta, 7, 283 (1955).
- (4) G. R. Lachance, R.J. Traill, Canadian Spectroscopy, 11, 43 (1966).
- (5) J.W. Criss, L.S. Birks, Analytical Chemistry, 40, 1080 (1968).
- (6) J. Ashe, Presented at NIST Workshop "Accuracy of Lead Measurements of Paint, Soil and Dust Samples by Laboratory-Based XRF", Peter Pella chairman, Boulder, CO, 1993.
- (7) Addendum to NIST Montana Soils Standard Reference Materials (2709, 2710, 2711) Analysis Certificate, 1993

## 12.0 Bibliography

1. Jenkins, R.; Gould, R. W.; and Gedcke, D. "Quantitative X-ray Spectrometry," New York: Marcel Dekker, Inc., 1975.
2. Berin, E.P. "Introduction to X-ray Spectrometry," New York: Plenum Press, 1978.
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5. Williams, K.L. "Introduction to X-ray Spectrometry," London: Allen & Unwin, 1987.
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7. de Vries, J.L.; Vrebo, B.A.R. "Handbook of X-ray Spectrometry", R.E. Van Grieken and A.A. Markowicz, eds., Chap. 5, Marcel Dekker (1993).

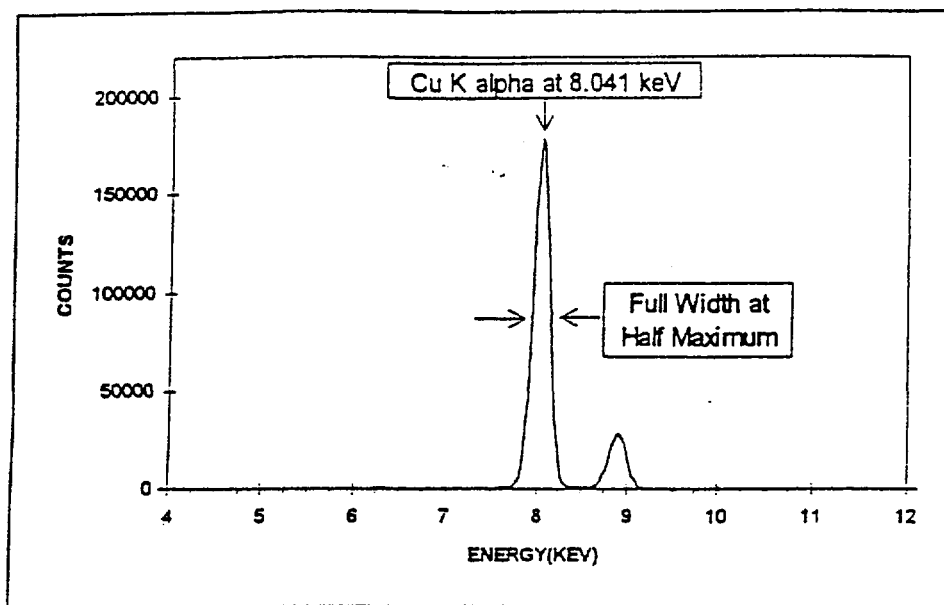


Figure 1. Spectrum of copper [Cu] calibration sample.

Sample ID	K %	CA %	TI %	CR PPM	MN PPM	FE %	NI PPM	CU PPM	ZN PPM	AS PPM	PB PPM	HG PPM	AG PPM	CD PPM	BA PPM	SIOS DIFF
2710	2.11	1.25	0.283	(39)	10110	3.38		2950	6952	626	5532	(32)	35	(22)	707	
2711	2.45	2.88	0.306	(47)	638	2.89		114	350	105	1162			42	726	
2704	2	2.6	0.457	135	555	4.11		99	438	(23)	161				414	
2709	2.03	1.89	0.342	130	538	3.5	88	35	106						968	
8408	(1.5)		(0.56)	(88)	(1400)	(2.6)			(160)		(80)	107			(360)	
8407	(1.7)		(0.44)	(98)	(970)	(2.42)			(230)		(96)	50			(400)	

Figure 2. Standards file data.

#### SPECTRUM PROCESSING- PROCEDURE 2- LOW Z STANDARDS

1. \*AR K - XML-FITTING < 2280 - 3660 EV >
2. K KA - XML-FITTING < 2640 - 4060 EV >
3. CA KA - XML-FITTING < 3000 - 4480 EV >
4. TI KA - XML-FITTING < 3820 - 5420 EV >
5. \*V KA - XML-FITTING < 4240 - 5920 EV >
6. CR KA - XML-FITTING < 4700 - 6440 EV >
7. MN KA - XML-FITTING < 5180 - 7000 EV >
8. FE KA - XML-FITTING < 5680 - 7560 EV >
9. \*BA L - XML-FITTING < 3480 - 6360 EV >

Figure 3. Reference file setup for Low Z standards.

#### SPECTRUM PROCESSING - PROCEDURE 3 MID Z STANDARDS

1.	*MN	- XML-FITTING	< 5300 - 6940 EV >
2.	*FE	- XML-FITTING	< 5880 - 7580 EV >
3.	*CO	- XML-FITTING	< 6260 - 8060 EV >
4.	NI KA	- XML-FITTING	< 6740 - 8780 EV >
5.	CU KA	- XML-FITTING	< 7300 - 9440 EV >
6.	ZN KA	- XML-FITTING	< 7880 - 10100 EV >
7.	AS KA	- XML-FITTING	< 9760 - 12420 EV >
Ø8.	PB LB	- XML-FITTING	< 9900 - 13480 EV >
Ø9.	*PBL	- XML-FITTING	< 8680 - 9660 EV >
Ø10.	*PBLG	- XML-FITTING	< 13840 - 16280 EV >
11.	*RB	- XML-FITTING	< 12560 - 15820 EV >
12.	*SR	- XML-FITTING	< 12980 - 16740 EV >
13.	*ZR	- XML-FITTING	< 14900 - 18580 EV >
14.	*BR	- XML-FITTING	< 11060 - 13960 EV >
15.	HG LB	- XML-FITTING	< 9300 - 13000 EV >
16.	*W LA	- XML-FITTING	< 7780 - 106600 EV >

Ø - Region No. 8 is defined using the interference sample spectrum

C:\REFS\SPECTRUM.199.

Ø - Regions Nos. 9 and 10 are defined using a pure Pb sample spectrum

C:\REFS\SPECTRUM.182.

Figure 4. Mid Z reference file setup.

#### SPECTRUM PROCESSING- PROCEDURE 4 HIGH Z STANDARDS

1.	AG KA	- XML-FITTING	< 21120 - 26120 EV >
2.	CD KA	- XML-FITTING	< 22120 - 27300 EV >
3.	SN KA	- XML-FITTING	< 24160 - 29840 EV >
4.	SB KA	- XML-FITTING	< 25220 - 31080 EV >
5.	BA KA	- XML-FITTING	< 30880 - 37980 EV >

Figure 5. High Z reference file setup.

## SPECTRACE INSTRUMENTS

SPECTRUM : NIST 2711

TUBE VOLTAGE : 10 KV  
TUBE CURRENT : 0.70 mA  
ATMOSPHERE : AIR

FILTER USED : ALUMINUM  
LIVETIME : 100 SEC

P.S. = 8K

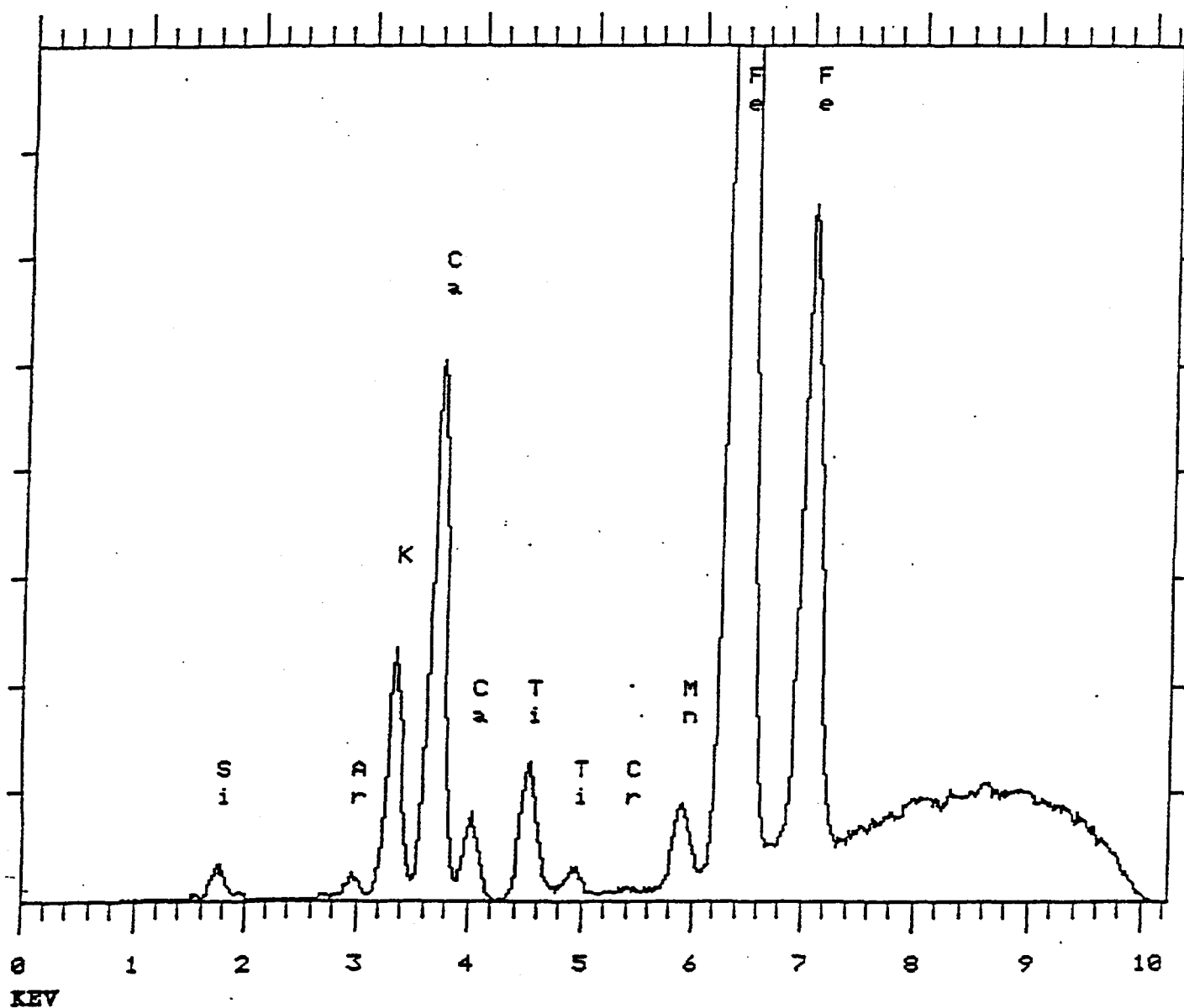


Figure 6. Example of a Low Z acquired spectrum.

## SPECTRACE INSTRUMENTS

SPECTRUM : 2711

TUBE VOLTAGE : 35 KV  
TUBE CURRENT : 0.10 mA  
ATMOSPHERE : AIR

FILTER USED : PD THICK  
LIVETIME : 200 SEC

P.S. = 2K

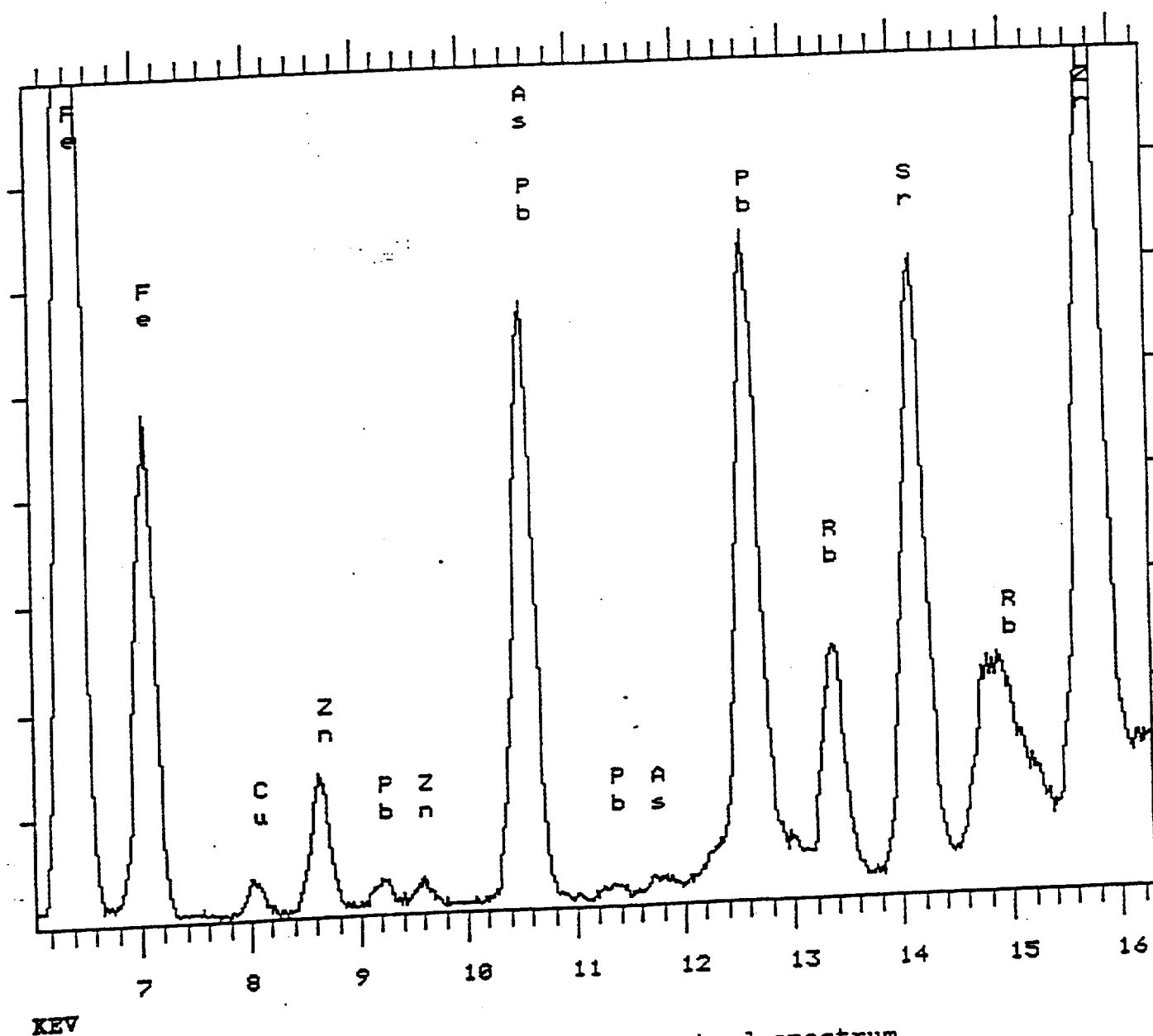


Figure 7. Example of a Mid Z acquired spectrum.



# SPECTRACE INSTRUMENTS

SPECTRUM : NIST 2711

TUBE VOLTAGE : 48 KV  
TUBE CURRENT : 0.10 mA  
ATMOSPHERE : AIR

FILTER USED : CU THIN  
LIVETIME : 200 SEC

F.S. = 4K

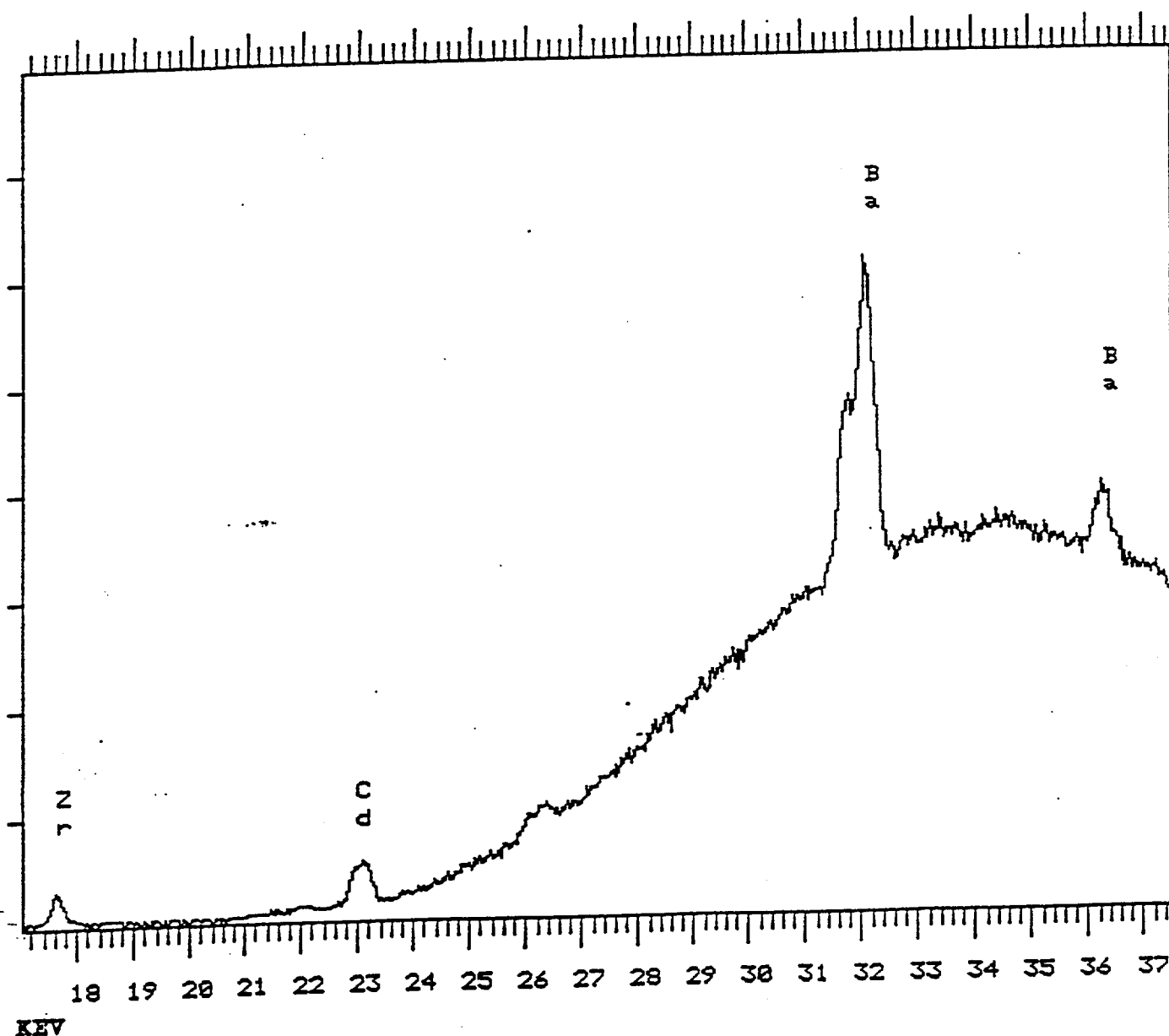


Figure 8. Example of a High Z acquired spectrum.

EDXRF ANALYSIS  
SPECTRACE INSTRUMENTS

PROCEDURE : LOW Z UNKNOWN  
 FILTER USED : ALUMINUM  
 ATMOSPHERE : AIR  
 COUNT RATE RANGE : MED  
 ANALYSIS METHOD : NO ANALYSIS  
 TUBE VOLTAGE : 10 KV  
 TUBE CURRENT : 0.70 MA  
 LIVETIME : 100 SEC  
 PRESET COUNT : 0 K  
 TIME : 1:03 pm  
 DATE : 5/16/96

EDXRF ANALYSIS  
SPECTRACE INSTRUMENTS

PROCEDURE : MID Z UNKNOWN  
 FILTER USED : PD THICK  
 ATMOSPHERE : AIR  
 COUNT RATE RANGE : MED  
 ANALYSIS METHOD : NO ANALYSIS  
 TUBE VOLTAGE : 15 KV  
 TUBE CURRENT : 0.12 MA  
 LIVETIME : 200 SEC  
 PRESET COUNT : 0 K  
 TIME : 1:03 pm  
 DATE : 5/16/96

EDXRF ANALYSIS  
SPECTRACE INSTRUMENTS

PROCEDURE : HIGH Z UNKNOWN  
 FILTER USED : CU THIN  
 ATMOSPHERE : AIR  
 COUNT RATE RANGE : MED  
 ANALYSIS METHOD : PEAK RATIOS  
 TUBE VOLTAGE : 48 KV  
 TUBE CURRENT : 0.10 MA  
 LIVETIME : 200 SEC  
 PRESET COUNT : 0 K  
 TIME : 1:03 pm  
 DATE : 5/16/96

EDXRF ANALYSIS  
SPECTRACE INSTRUMENTS

PROCEDURE : COMBINATION 2+3+4  
 FILTER USED : PD MEDIUM  
 ATMOSPHERE : AIR  
 COUNT RATE RANGE : MED  
 ANALYSIS METHOD : FUN. PARAMS.  
 TUBE VOLTAGE : 30 KV  
 TUBE CURRENT : 0.02 MA  
 LIVETIME : 100 SEC  
 PRESET COUNT : 0 K  
 TIME : 1:04 pm  
 DATE : 5/16/96

SAMPLE	ELEMENT	CONCENTRATION	ERROR
335	K	2.528 %	+/- 0.0203
	CA	1.031 %	+/- 0.0103
	TI	0.177 %	+/- 0.0032
	CR	11.347 PPM	+/- 8.7141
	MN	1047.719 PPM	+/- 12.9442
	FE	6.713 %	+/- 0.0078
	NI	33.321 PPM	+/- 3.5587
	CU	2268.150 PPM	+/- 17.4263
	ZN	2157.262 PPM	+/- 15.0266
	AS	192.295 PPM	+/- 1.9042
	PB	271.172 PPM	+/- 4.3691
	HG	N D	
	AG	9.647 PPM	+/- 0.8334
	CD	6.495 PPM	+/- 0.9373
	BA	675.437 PPM	+/- 10.6193
	SIO5	88.882 DIFF	

Figure 9. Example of a Spectrace QuanX sample printout.

RUN #	FWHM*	PEAK CENTROID	TOTAL COUNTS	PEAK COUNTS	TIME
1	180.1	8041	2187969 ± 0.00%	1345906 ± 0.00%	12:30:28
2	179.5	8042	2189712 ± 0.04%	1346270 ± 0.01%	12:38:01
3	179.7	8042	2188745 ± 0.03%	1344938 ± 0.04%	12:45:28
4	179.6	8042	2187722 ± 0.04%	1344136 ± 0.06%	12:52:55
5	179.3	8042	2189506 ± 0.04%	1347528 ± 0.09%	13:00:22
6	179.0	8042	2189264 ± 0.03%	1345296 ± 0.08%	13:07:50
7	179.8	8042	2186424 ± 0.05%	1343684 ± 0.09%	13:15:16
8	179.3	8042	2194782 ± 0.11%	1350504 ± 0.15%	13:22:44
9	179.4	8042	2191210 ± 0.10%	1347079 ± 0.14%	13:30:12
10	179.1	8042	2191683 ± 0.10%	1347479 ± 0.14%	13:37:39

\*- FWHM - full width at half maximum of the Cu K alpha peak. See Figure 1.

Figure 10. Example of resolution and stability test procedure printout.

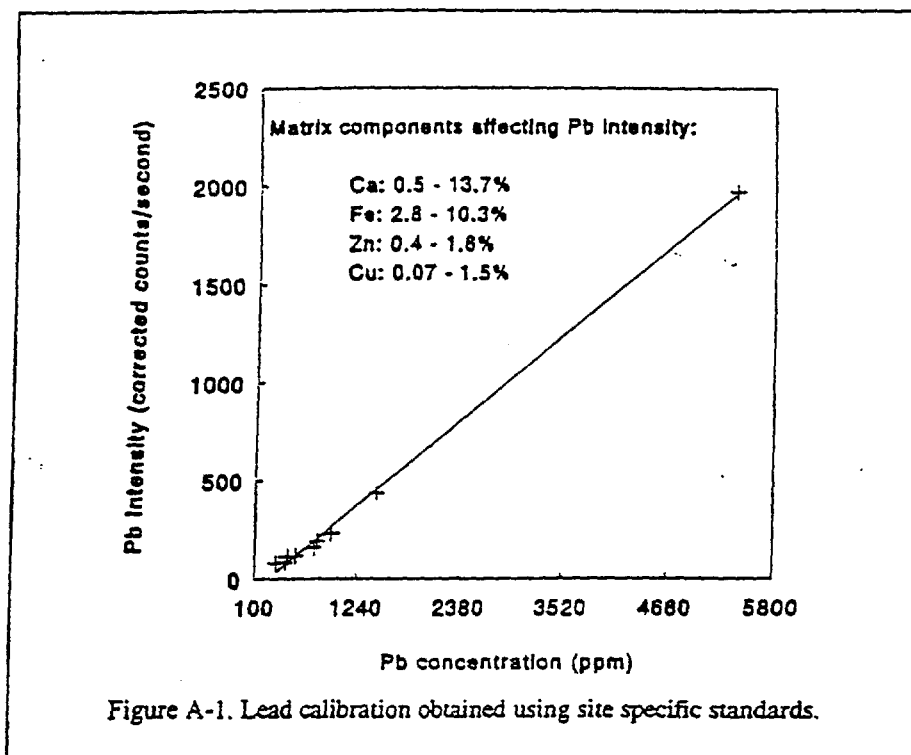
Government agencies as well as private industry are actively investigating and remediating soils at sites contaminated by heavy metals. Energy dispersive X-ray fluorescence analysis (EDXRF) is well suited to the determination of heavy metals in contaminated soils because it is a non-destructive and accurate elemental analysis technique. Energy dispersive X-ray fluorescence spectrometers are field portable or transportable in a van or trailer. Transportable EDXRF systems can provide minimum detectable levels (MDL) below 10 ppm for most metals. Field portable EDXRF instruments provide MDLs below 50 ppm for most metals. EDXRF results correlate well with other metal analysis methods (AA or ICP).

Quantitative X-ray fluorescence analysis is a comparison analytical method; EDXRF spectrometer response for an elemental emission line is evaluated with respect to the known concentration of the element in a standard material. Simple sample matrix types such as polymers or hydrocarbons, exhibit linear X-ray intensity response over limited metal concentration ranges. Contaminated soils, by comparison, are complex samples in regard to their overall elemental composition. Matrix effects are defined as the impact that the concentration variations of major soil components (ex. Ca, Fe, Si) has on measured analyte X-ray emission intensity.

Matrix effects produce a non-linear measured X-ray intensity versus metal concentration response when analyzing soils. A classical method that addresses matrix effects, called site specific standardization, relies on a suite of standards and regression mathematics. When this aspect of EDXRF is applied to contaminated soils analysis several concerns arise as listed in Table A-1. The standard materials selected for EDXRF calibration must contain metal analyte concentrations that bracket the range found at the contaminated site. In addition, the concentrations of iron, calcium, and silicon in the standard materials must bracket those found in the soil types at the site.

Table A-1. Comparison of two standardization methods.	
FP Standardization	Site Specific Standardization
<input type="checkbox"/> No site sampling required prior to project initiation;	<input type="checkbox"/> Soil samples to be used as standards must be collected well in advance of project initiation date;
<input type="checkbox"/> Pure elements and/or readily available certified reference materials are used as standards (see Appendix B);	<input type="checkbox"/> High costs associated with lab analysis of soils and significant time required to receive data back;
<input type="checkbox"/> Concentration levels of matrix and metals in the standards need not bracket the levels found at the site.	<input type="checkbox"/> A large number of standards are required so that the matrix and metal concentrations bracket the entire range found at the site.

Figure A-1 is an example of a site specific standardization for lead in soil. The samples earmarked to be used as standards were collected during an expeditionary sampling trip to the site followed by independent analysis of the collected samples. Soil samples selected as standards (usually significantly fewer than were collected) are designated "site specific" and hopefully bracket the concentration ranges required. Some reasons for omitting a soil sample from the suite of standards may include: (1) Having several other samples possessing the same general concentrations of metals and matrix, or (2) questionable independent analysis data for a metal or matrix component.



Generating site specific standards may be prohibitive for two reasons: (1) Cost considerations concerning expeditionary sampling and sufficient independent analysis to have confidence in the soil metal and matrix compositions, or (2) time constraints involving sampling and waiting for independent analysis results.

The Pb calibration curve shown in Figure A-1 is only valid if unknown soil compositions fall between 400 and 5200 ppm Pb and possess a matrix makeup in the ranges listed on the figure. While at some sites this requirement may be met, other sites may provide samples that routinely fall outside the required concentration ranges.

As a result of the constraints imposed by site specific standardization, a mathematical treatment of matrix effects designated "Fundamental Parameters" (FP) has been developed (see Table A-1). The FP routines discussed in this report provide accurate metal concentration determinations in contaminated soil samples that have wide ranges of metal and matrix concentrations. Calibration of an FP method requires only a limited set of certified generic soil standards or pure elements.

The Spectrace models 6000 and 5000 use X-ray tube excitation and the FP routine is classified as a tube modeling routine.

## TUBE MODELING FP ROUTINES

Fundamental parameter routines based on tube modeling use equations describing X-ray tube intensity output distributions. Mathematical derivation of these algorithms occurred sometime ago; they have only recently been executed on personal computers.

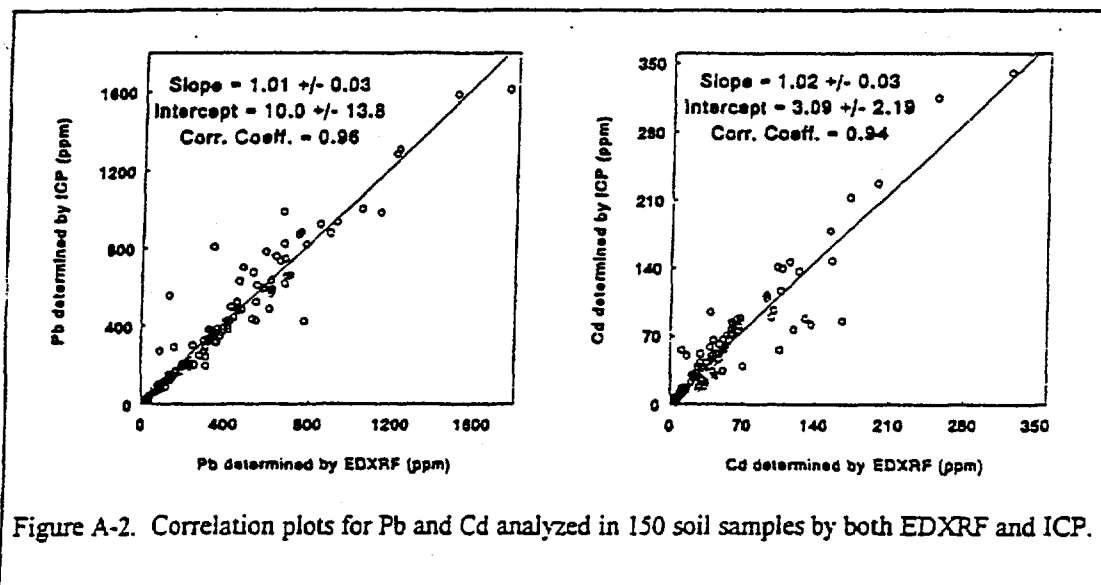
Tube modeling routines can use pure elements or oxides of the pure elements as standards. Unfortunately, however, X-ray excitation conditions appropriate for analysis of a pure metal sample do not result in optimum sensitivities and minimum detectable metal levels in a soil matrix.

To achieve optimum X-ray analysis conditions for metals in soils, a limited set (typically six) of soil standard materials is selected. The National Institute of Standards and Technology (NIST) provides several certified reference materials satisfactory for standardization of the tube modeling FP routines.

Prior to FP standardization X-ray spectra of the standards are collected and analyzed for analyte and matrix element emission intensities. Calibration proceeds by completely defining for the program each standard sample's composition, including the major components (ex. Fe, Ca). Many instances arise when a portion of the matrix may be better estimated by a difference component. For soil, the difference component is defined as  $\text{SiO}_X$  where X can be 2 - 5. When X = 5, a composition of 24% Si and 45% O results that approximates the concentrations found in most soils types.

The tube output distribution is calculated by the program followed by determination of the matrix independent pure element count rate (PECR) for each analyte. The routine then develops a set of theoretical standards. Next, the routine computes the theoretical X-ray intensity expected for each analyte using equation 2.1 in the Spectrace 5000/6000 Standard Operating Procedure (SOP). Combining the theoretical standard and intensity information, alpha influence coefficients are determined by solving simultaneous equations of the form in equation 2.2 in the SOP. Alpha coefficients describe the quantitative effect of each matrix element on an analyte's measured X-ray intensity.

Unknowns are quantitated by estimating analyte concentration from the measured intensity and the alpha coefficients. Next, theoretical intensities are calculated from equation 2.1 and then the computed intensities are compared with the measured intensities. If the intensities are more than 1% different, a new estimate of concentration is made and the theoretical intensity computation is repeated. The iteration continues until the theoretical and measured intensities converge. Figure A-2 illustrates correlation between a tube modeling FP routine for 150 soil samples analyzed by EDXRF for Pb and Cd and inductively coupled plasma analysis (ICP) data.



## CONCLUSION

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The incorporation of fundamental parameter routines for EDXRF analysis of soils provides accurate estimates of metal contaminant concentration with a minimum number of standard materials. FP standardization offers several advantages when compared with site specific standardization. Fundamental parameters standardization relies on pure element standards or certified standard reference soil materials. These materials are readily available, unlike site specific standards. Universal application to all soil matrix types is another merit of FP standardization. When analyzing soil samples collected from a site EDXRF results correlate well with AA and ICP methods. Fundamental parameters analysis methods provide rapid and cost effective EDXRF measurement data in contrast to site specific standardization that requires an initial sampling trip and the time interim waiting for laboratory results.

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**TECHNICAL STANDARD OPERATING PROCEDURE  
XRF INSTRUMENT OPERATION**

**ATTACHMENT B**

**Soil Analysis Application Report  
Low Concentration Soil Contaminant Characterization Using EDXRF Analysis**





# LOW CONCENTRATION SOIL CONTAMINANT CHARACTERIZATION USING EDXRF ANALYSIS

AR. Harding

## INTRODUCTION

Effective assessment and remediation of hazardous waste sites dictates that analytical methodologies be developed which assist in the evaluation of site contamination and simultaneously make efficient use of sampling time and resources (1). Optimally, a technique would provide on-site personnel with immediate and accurate information concerning the identity and concentration of inorganic soil contaminants (2).

Inorganic pollutants can be readily determined in contaminated soils with energy dispersive X-ray fluorescence spectrometry (EDXRF) using a thermoelectrically cooled Si(Li) detector (3). A field mobile laboratory van or trailer can accommodate the EDXRF system because the electrically cooled detector, which provides high resolution EDXRF spectra, does not require cryogenic cooling. Soil sample preparation for EDXRF analysis is minimal, therefore, short turnaround times are realized between sampling and reporting results.

This report will describe an EDXRF method developed to determine four inorganic soil contaminants: lead, arsenic, zinc, and cadmium at four sampling depths. The EDXRF results for approximately one hundred eighty soil samples will be compared to results obtained for sample splits submitted for analysis at an independent laboratory. Evaluation of low concentration arsenic detectability with elevated lead concentrations in these samples will be discussed. Accuracy and precision of the EDXRF method will also be compared to the independent methods using a standard reference material and soil samples submitted in triplicate to both laboratories.

## EXPERIMENTAL

The field mobile EDXRF spectrometer used in this work was a Spectrace 6000 (Spectrace Instruments, Inc., Mountain View, CA). The EDXRF system consists of three modules: the spectrometer, the control/pulse processing electronics, and the data analysis computer. The compact size and weight (90 lbs.) of the modules permits installation of the system in a laboratory trailer or van.

The bench top spectrometer module, which can accommodate a single soil sample, is powered by 110 V line or generator feed. The excitation source used is a low powered Rh anode X-ray tube (50 KV, 0.35 mA (17 W) maximum output) positioned at a 45° incident angle to the sample. Three primary radiation filters permit optimum spectral acquisition conditions to be computer selected.

The thermoelectrically cooled Si(Li) X-ray detector is mounted at a 45° take-off angle in an inverted geometry with respect to the sample. The 20 mm<sup>2</sup> Si(Li) crystal, which is protected by a 0.5 mil Be window, is cooled to -90°C for operation using a multi-stage thermoelectric (Peltier effect) cooler. The 300 watts produced at the detector heat sink are dissipated by forced ambient air. Thermoelectrically cooled detectors provide typical resolutions of 185 eV (Mn Ka).

A card cage module is interfaced between the spectrometer and a personal computer. The card cage components include the detector high voltage supply, the pulse processing electronics, and the control circuit board for the EDXRF spectrometer. The data analysis software executed on the PC is capable of either a fundamental parameters or empirical data treatment scheme using a combination of standard reference materials and/or site specific standards.

Sampling of the suspected waste site was performed using EPA approved protocols in a 9500' x 3500' rectangular area. Forty-three (43) cores were collected and partitioned into four depth levels: surface to 2"; 2" to 6"; 6" to 12"; and 12" to 18", and designated levels 1 through 4, respectively. At the site, samples were first homogenized and then split into two fractions. One was submitted for EDXRF analysis and the other sent to an independent lab for analysis.

The independent laboratory used EPA SW 846 (methods 3050 and 6010) methodology to determine Cd, Pb, and Zn concentrations in the soil sample splits. Arsenic was determined in those splits using SW 846 method 3050 and EPA method 206.4 (spectrophotometric).

Sample preparation for EDXRF analysis consisted of drying the sample for 4 minutes in a microwave oven followed by sieving the dried sample. Material passing through the 2 mm sieve was collected as sample and was free of large foreign objects such as pebbles and sticks. Drying the sample was required due to the variable moisture content in the submitted soils; some surface samples had the consistency of mud. The sieved soil was then ground in a Spex shatterbox grinder (Spex Ind., Edison, NJ) using tungsten carbide cups for 2 minutes. Grinding cups were subsequently cleaned using soap and tap water. The cleaned cups were rinsed with distilled/deionized water followed by isopropanol. Approximately 5 grams of prepared sample were poured into a disposable 32 mm X-ray sample cup and covered with a 6.3  $\mu$ m polypropylene film. Five grams of dried sample gave the equivalent of a 15 mm sample depth in the cup. Approximately twenty-five samples were prepared and analyzed per day.

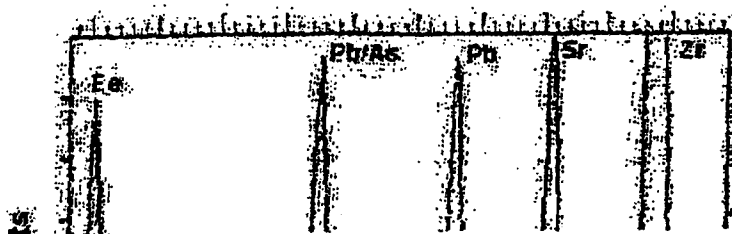
## STANDARDIZATION METHOD

Two sets of excitation conditions were employed to determine seven elements in the soil samples, four of which are of specific environmental concern: Zn, As, Pb, and Cd. Table 1 lists the two sets of spectral acquisition conditions and which conditions were used to determine each analyte.

SPECTRAL REGION	CONDITIONS	ANALYTES
MID Z	35 KV, 0.35 mA, 0.13mm Rh filter, 200 s livetime	Mn, Fe, Cu Zn, Pb, As
HIGH Z	50 KV, 0.35 mA, 0.63mm Cu filter, 200 s livetime	Cd

Table 1. Spectral acquisition conditions for the EDXRF analysis of soils.

Figure 1 is a mid Z spectrum of a soil sample that was found to contain 125 ppm As, 1100 ppm Pb, and 729 ppm Zn. A multiple linear least squares peak fitting routine was used for deconvolution of overlapped peaks.



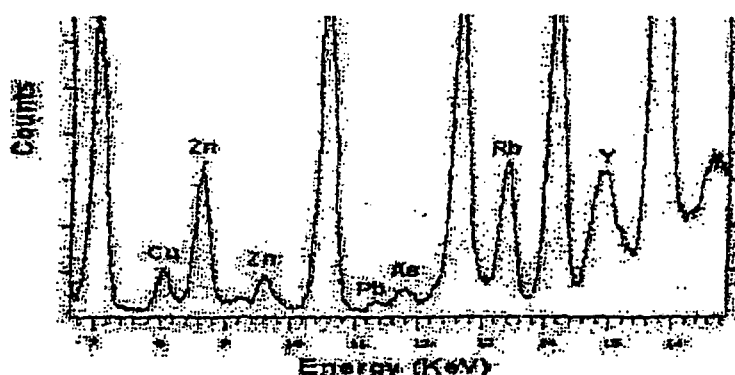


Figure 1. Mid Z spectrum of a soil sample containing 1100 ppm Pb, 729 ppm Zn, and 125 ppm As. Full scale on the y-axis is 2,000 counts.

The soil characterization method was standardized using four standard reference materials (SRM): NBS 1648 (urban particulate); NBS 2704 (river sediment); SO- 1 and SO-3, two soil standards available from the Canada Centre for Mineral and Energy Technology. Standards labeled NBS are available from the National Institute for Standards and Technology (NIST). These SRMs have certified concentrations of Fe, Mn, Cu, Zn, Pb, and Cd.

A fundamental parameters (FP) method (5) was employed as the data treatment scheme and used certified concentrations of Fe, Mn, Cu, Zn, Pb, and Cd in the four standard materials. To compute instrumental sensitivity (emission peak counts per second per ppm), the balance of the standard was assumed to be comprised of SiO<sub>2</sub> to account for the contribution of the matrix on the measured analyte X-ray intensity. The balance component SiO<sub>5</sub> was selected to mimic the concentration of Si and O in typical soils, approximately 24% Si and 45% O. Since none of the selected SRMs contain arsenic, As sensitivity (cps/ppm) was determined using a fundamental parameters theoretical calculation based on the computed Zn sensitivity. Table 2 lists the analyte sensitivities computed by the FP method.

ANALYTE	SENSITIVITY (cps/ppm)	LLD (ppm)
Mn	0.010	21
Fe	0.015	19
Cu	0.046	26
Zn	0.067	19
Pb	0.084	7
As	0.132	12
Cd	0.107	4

Table 2. Sensitivity and lower limits of detection for the analytes of interest.

There are some advantages to using an FP method for standardization compared to site specific soil standards. The FP method can use readily available, well-characterized SRMs to measure analyte sensitivities. Site specific soil standards, by contrast, are usually collected with a separate sampling mobilization. The FP method standardized with SRMs can provide accurate analyte concentrations to be determined in samples with fairly wide matrix variations without restandardization, unlike methods incorporating site specific standards.

## RESULTS

Table 2 lists the lower limits of detection determined using the two sets of spectral acquisition conditions (Table 1). The pertinent equation is:  $LLD (ppm) = 3 \cdot \sqrt{I_b} / m \cdot \sqrt{T}$ , where  $I_b$  is the background intensity (cps),  $m$  is the analyte sensitivity (cps/ppm), and  $T$  is the acquisition livetime in seconds (6). Calculated LLD values are dependent upon spectrum acquisition times, sample matrix, and excitation conditions. The conditions in Table 1 were selected to optimize the Pb and Cd spectral regions. Improved LLDs are possible with EDXRF using longer spectrum acquisition livetimes and optimized excitation conditions for selected spectral regions.

Results for the determination of four analytes by EDXRF in 180 samples (43 cores at 4 levels, two SRMs, three samples in triplicate) were compared to independent analysis results in order to evaluate the level of agreement between the two methods. Table 3 lists the correlation plot data for the analytes in terms of actual slope, intercept, errors, and the correlation coefficient of the fit. Each analyte correlation plot included approximately 150 data points.

ANALYTE	SLOPE	INTERCEPT	CORRELATION COEFFICIENT
Pb	$1.01 \pm 0.03$	$10.0 \pm 13.8$	0.96
As	$1.08 \pm 0.05$	$0.98 \pm 3.54$	0.92
Cd	$1.02 \pm 0.03$	$3.09 \pm 2.19$	0.94
Zn	$1.02 \pm 0.02$	$63.0 \pm 13.6$	0.98

Table 3. Correlation plot data for the four analytes of environmental interest.

As shown in Table 3, slopes of the plots for Pb, Cd, Zn, and As are within 8% of 1.00 and all correlation coefficients are greater than 0.92. The calculated slope near 1.00 and correlation coefficients greater than 0.90 indicates agreement between the two analytical techniques. Figure 2 is a plot of 94 data points in the range of 0 to 300 ppm Pb. Figure 3 is a plot of 110 EDXRF and ICP analyzed samples in the range of 0 to 100 ppm Cd and also indicates agreement between the results of the two methods.

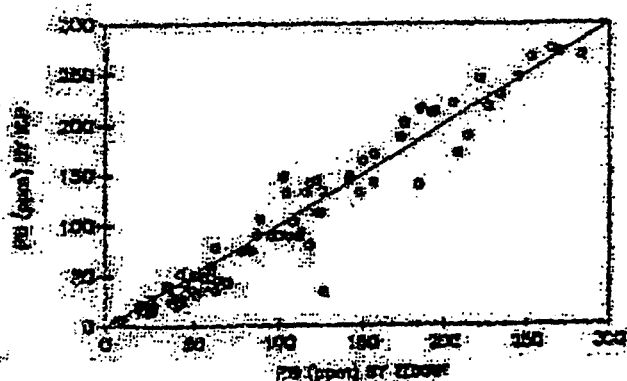


Figure 2. Pb correlation plot for 94 samples.



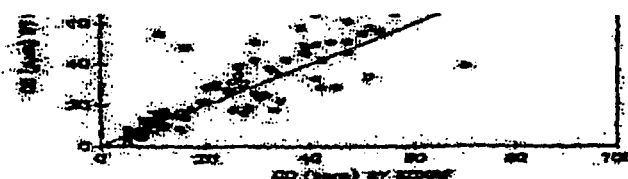


Figure 3. Cd correlation plot for 110 samples.

## ACCURACY AND PRECISION

To evaluate the accuracy provided by the EDXRF method two SRMs were submitted as unknowns for EDXRF analysis as well as being submitted to the independent lab for analysis. Table 4 lists the results for SRM SO-2. EDXRF analysis of SO-2 provides results that are in good agreement with certified values. The independent ICP analysis of zinc in SO-2, however, is biased low by a factor of one-half.

Sample	Analyte	ICP	EDXRF	Certified
SO-2	Pb	19	17	21
	Zn	55	123	124

Table 4. Results of the analysis of SRM SO-2 by ICP and EDXRF methods. All values in ppm.

Precision was evaluated by submitting three samples a total of three times for independent and EDXRF analysis. Table 5 shows the results for the two methods along with the calculated standard deviation (in ppm) of the three replicate analyses. Note that Cd in sample C was only reported by EDXRF to the nearest 1 ppm and three values of 9 ppm Cd were determined, hence the zero standard deviation for the three replicates. EDXRF precision is better than 10% relative standard deviation in all but one case (As in sample C) and compares well with that provided by the independent lab.

Sample	Element	Ind. Lab	EDXRF
A	As	45 ± 4	41 ± 3
	Cd	20 ± 2	31 ± 3
	Pb	286 ± 26	312 ± 12
	Zn	185 ± 15	134 ± 10
B	As	17 ± 3	14 ± 1
	Cd	80 ± 6	58 ± 4
	Pb	141 ± 15	158 ± 3
	Zn	556 ± 39	529 ± 46
C	As	17 ± 1	19 ± 4
	Cd	10.0 ± 0.9	9 ± 0
	Pb	117 ± 8	142 ± 14
	Zn	173 ± 26	128 ± 3

Table 6. EDXRF and independent lab results for three soil samples each analyzed in triplicate. All values in ppm

## CONCLUSION

Field mobile EDXRF analysis of soils suspected of being contaminated provides information concerning the nature, extent, and magnitude of the contamination. Due to the minimal sample preparation necessary for EDXRF analysis, sampling to result turnaround time is relatively short so

preparation necessary for EDXRF analysis, sampling to result turnaround time is relatively short so the most effective use of sampling resources is realized. EDXRF detection limits below 20 ppm were obtained for the elements of environmental concern. The effect of increasing lead concentration on arsenic detectability was quantified. Using the EDXRF method described here, reliable As results were found for those samples containing As/Pb concentration ratios above 0.083. Accuracy and precision for the analytes of interest using the EDXRF method was shown to be comparable to results obtained by independent analysis. Comparable results for Cd, As, Pb, and Zn between independent and EDXRF methods validates the use of EDXRF analysis for hazardous waste site investigation and remediation.

## ACKNOWLEDGMENT

The author would like to acknowledge James P. Walsh and Associates for site sampling and providing the independent analysis data.

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Last modified: 11/02/98